Research Article

Deuterium kinetic isotope effects and H/D exchange in dimerization of acetylene with a Nieuwland catalyst in aqueous media

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Deuterium kinetic isotope effects were observed in the dimerization of acetylene with a Nieuwland catalyst in an aqueous media, where the copper–acetylene and copper–monovinylacetylene (MVA) π-complexes were detected as intermediates by ^{1}H NMR. The copper–acetylene π-complex is responsible for an efficient H/D exchange between acetylene and proton (or deuteron) of water, which occurs rapidly with a Nieuwland catalyst. The deuterium kinetic isotope effects and the rapid H/D exchange reaction together with the detection of the copper–acetylene and copper–MVA π-complexes provide deeper insight into the catalytic mechanism of the Nieuwland catalysis for the dimerization of acetylene. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: deuterium kinetic isotope effect; copper complex; acetylene; Nieuwland catalyst

INTRODUCTION

Alkyne and alkene complexes of transition metals are potential intermediates in a variety of catalytic reactions of C—C bond formation which are relevant for important industrial processes.[1–7] In particular, a Nieuwland catalyst composed of CuCl and KCl or NH_4Cl in an aqueous media has long been the representative catalyst for the acetylene dimerization on an industrial scale.[8–11] Such an aqueous catalytic system is environmentally favorable as compared with those in organic solvents.[12,13] The dimerized product of acetylene, monovinylacetylene (MVA) is readily converted to chloroprene,[14] which is an important starting material for the synthetic rubber.[15] Chloroprene rubber has many superior characteristics compared to natural and even other synthetic rubber types. Despite such practical importance and a long history of the Nieuwland catalyst, there have been only a few reports on the mechanistic study.[16,17] The copper–acetylene complex $Cu(C_2H_2)^+$, which may be a potential intermediate for the catalytic dimerization of acetylene, has been detected in the gas phase,[18–21] and the quantum chemical study of the structure and bonding of copper–acetylene complexes has been reported.[22–25] The wide diversity of possible bonding motifs of the alkynyl moiety has stimulated the design and synthesis of copper alkynyl complexes as metal-based functional materials.[26–30] However, a great care is needed to avoid formation of explosive copper acetylide and ignition of divinylacetylene (DVA) formed as a by-product with oxygen. This has precluded the detailed study on the direct detection of a copper–acetylene complex intermediate in relation with the kinetics of the catalytic dimerization of acetylene. In the industrial process, the catalytic reaction is carried out in deoxygenated aqueous solutions containing high concentrations of CuCl and KCl or NH_4Cl under proper pH range to inhibit the formation of explosive copper acetylide and the reactions with oxygen.

A kinetic study on the dimerization of acetylene in water was performed under similar reaction conditions as the industrial Nieuwland catalytic process of the dimerization of acetylene by assuming that the rate-controlling step is a second-order reaction of an activated catalyst with acetylene or water.[17] However, the kinetic order has yet to be confirmed. On the other hand, we have recently reported the detection of the copper–acetylene and copper–MVA π-complexes by ^{1}H NMR and the occurrence of H/D exchange under virtually the same reaction conditions as the industrial Nieuwland catalytic process of the dimerization of acetylene.[31,32] The role of the π-complexes on the H/D exchange has yet to be clarified.

We report herein the first detailed kinetic analysis of the consumption of the reactant, the intermediates and the products in solution as well as in the gas phase including deuterium kinetic isotope effects for the dimerization of acetylene with a Nieuwland catalyst. The results obtained in this study have enabled us to clarify the role of the π-complexes on the H/D exchange, providing deeper insight into the catalytic mechanism

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of the dimerization of acetylene as well as improvement of the industrially important process.

EXPERIMENTAL

An aqueous solution of a Nieuwland catalyst (50 mL) was prepared by mixing CuCl (34.65 g, 0.350 mol) and KCl (24.80 g, 0.333 mol) in 29.9 mL of distilled water at 343 K under nitrogen stream and stirred for 30 min. Acetylene was synthesized by Denki Kagaku Kogyo Co. Ltd. MVA was obtained by acetylene dimerization with a Nieuwland catalyst. DVA was a minor product of acetylene dimerization, and separated by extraction. They were all used without further purification. First, the time course of the products released to the gas phase was monitored by GC at 323 K. After flowing acetylene into the catalyst solution for 15 min, the gas phase was flushed with nitrogen stream and the flask was sealed. Under the present experimental conditions, the catalyst solution remains homogeneous. The reactant and products in the gas phase were analyzed every 30 min by GC (Shimadzu GC-14A equipped with a thermal conductivity detector and a DEGS Chamelite FK chromatography column). The gas phase was also analyzed by GC-MS (Shimadzu GCMS-QP5000 equipped with a DB-1 chromatography column). ^{1}H-NMR spectra were recorded at 323 K on JEOL GSX-400 spectrometer. After bubbling acetylene, a capillary tube to evaluate quantitatively was inserted into the NMR tube. The capillary tube contained 1000 ppm of TSP (3-(trimethylsilyl) propanesulfonic acid, sodium salt) as an internal standard

and D_2O as a solvent. The number of scans was 64 times for 7 min, and the average time of each scan was defined as a reaction time. The prepared samples were measured at every 15 min for keeping intended temperatures. After 2 h from measurement, the interval was 30 min. ^{1}H NMR spectra of 1-pentyne with the Niuewland catalyst were also measured in the presence of 0–20 mL of a DCl aqueous solution (2.4 M).

RESULTS AND DISCUSSION

The time course of the products released to the gas phase was monitored by GC with time course at 323 K. After flowing acetylene into the catalyst solution for 15 min, the gas phase was flushed with nitrogen stream and the flask was sealed. Under the present experimental conditions, the catalyst solution remains homogeneous.[16] The reactant and products in the gas phase were analyzed every 30 min by GC. The results are shown in Fig. 1a, where the amount of acetylene detected in the gas phase decreases, accompanied by formation of MVA, which is then converted to DVA. When H_2O was replaced by D_2O, the rate of disappearance of acetylene as well as the rate of formation of MVA decreases significantly as compared with the corresponding rate in H_2O as shown in Fig. 1b. In both cases, the rate of disappearance of acetylene obeys first-order kinetics as indicated by the linear first-order plots in Fig. 1c. The deuterium kinetic isotope effect is determined to be 4.7 from the slopes in Fig. 1c. The observation of such a significant deuterium kinetic isotope effect between the reactions in H_2O and D_2O suggests
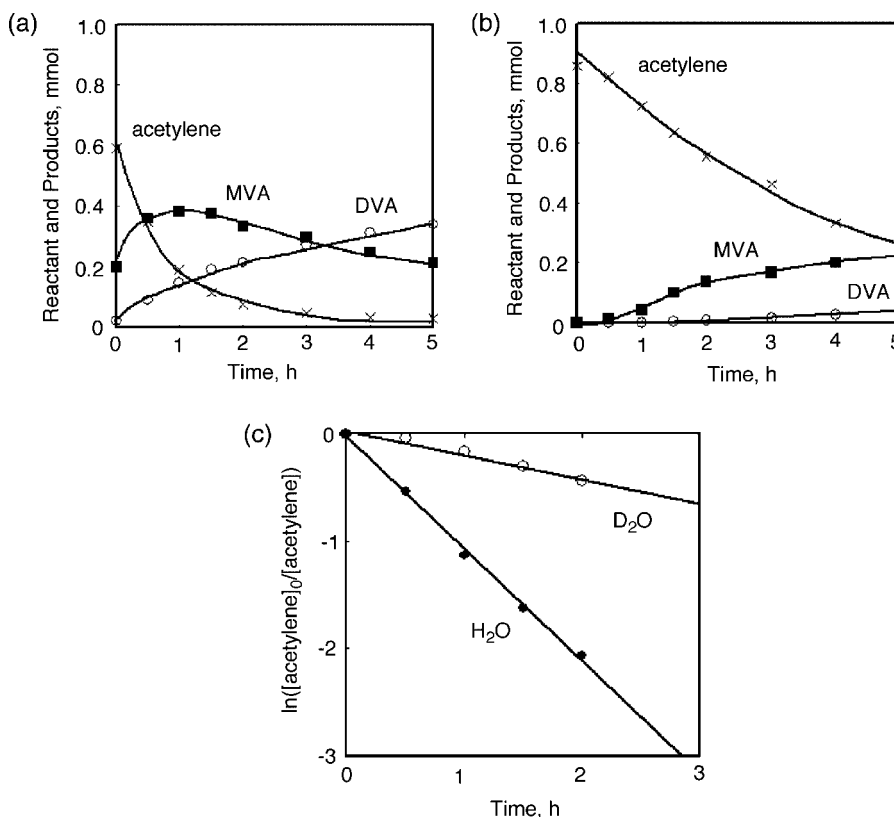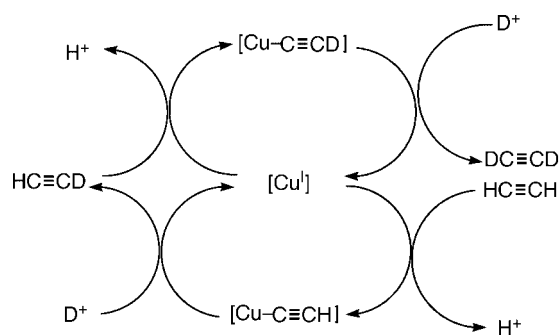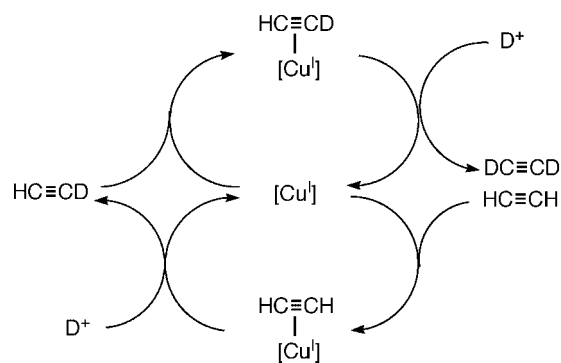

Figure 1. Time profiles of consumption of acetylene ($\times$) and formation of products [MVA($\blacksquare$) and DVA ($\bigcirc$)] detected in the gas phase in the reaction of acetylene with a Nieuwland catalyst ([CuCl] $= 7.0$ M) (a) in H_2O and (b) in D_2O at 323 K. (c) First-order plots in H_2O and D_2O

Scheme 1.

Scheme 2.

that water is involved in the dimerization of acetylene with the Nieuwland catalyst.

When GC-MS spectra of acetylene in the gas phase were measured at the beginning of the reaction (15 min), it was found that a rapid H/D exchange between acetylene and water occurred with the Nieuwland catalyst (*vide infra*). The GC-MS spectrum of HC≡CH in the gas phase of a H_2O solution of acetylene/Nieuwland catalyst exhibited a peak at $m/z = 26$ detected when H_2O is replaced by D_2O, an H/D exchange of acetylene with D_2O occurs to afford HC≡CD ($m/z = 27$) and DC≡CD ($m/z = 28$). The occurrence of H/D exchange between acetylene and proton (or deuteron) in water suggests that deprotonation of acetylene is involved in the Nieuwland catalysis to produce a σ-complex of deprotonated acetylene with Cu^I species that is in equilibrium with acetylene as shown in Scheme 1.[15] In D_2O, HC≡CH is converted to HC≡CD and then to DC≡CD probably via a σ-complex of deprotonated acetylene with Cu^I species in Scheme 1 where the catalytically active species is shown in the parenthesis: [Cu—C≡CH(orD)]. The observation of a significant deuterium kinetic isotope effect (KIE = 4.7) in the catalytic dimerization also suggests that the deprotonation of acetylene to produce a σ-complex of deprotonated acetylene with Cu^I species is involved in the rate-determining step. However, the H/D exchange occurs prior to the dimerization of acetylene, because C_2H_2 was already converted to C_2D_2 at 15 min after introduction of (a) C_2H_2 into a H_2O solution of the Nieuwland catalyst (Fig. 1b), when no dimerization product (MVA) was produced. Thus, the catalytically active species for the H/D exchange reaction should be different from that for the dimerization of acetylene (σ-complex of deprotonated acetylene with Cu^I species). Bohlmann *et al.* proposed the formation of π-complexes between the Cu^I ions and the triple bond, which would activate the alkyne toward deprotonation.[33] Such a π-complex formed between acetylene and Cu^I species of the Nieuwland catalyst may be responsible for the H/D exchange reaction between acetylene and water as shown in Scheme 2, whereas the σ-complex in Scheme 1 may be the active species for the dimerization of acetylene as discussed later.

In order to identify the reaction intermediates for the H/D exchange and the catalytic dimerization of acetylene, we measured the ^1H NMR spectra of the catalytic solution during the reaction. A catalyst solution was quickly added into an NMR tube to avoid depositing. Acetylene (the flow rate of 360 mL/h) was passed into an NMR tube for 3 min. The ^1H NMR measurements were performed on a JEOL GSX-400 spectrometer at 323 K. At 15 min, the large singlet signal is observed at
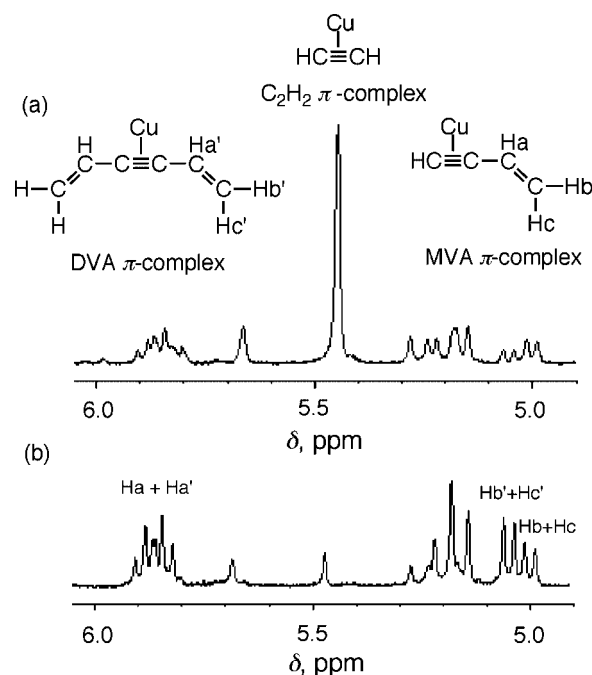

Figure 2. ^1H NMR spectra of the catalyst solution containing CuCl, KCl, and H_2O ([CuCl] = 7.0 M) at 323 K taken after passing acetylene (the flow rate 360 mL/h) for 3 min at (a) 15 min and (b) 360 min

$\delta = 5.45$ ppm which is assigned to the π-complex of acetylene with the Nieuwland catalyst (Fig. 2a), because a similar lower field shift of acetylene peak has been reported for the π-complex formation of acetylene with CuCl in HCl,[34] and also for other Cu^I–acetylene complexes.[35,36] It should be noted that there was no signal due to uncomplexed acetylene ($\delta = 2.35$ ppm). Thus, all acetylene molecules are converted to the π-complex with the Nieuwland catalyst. It should also be noted that no σ-complex of acetylene with the Nieuwland catalyst was observed during the dimerization of acetylene. As the acetylene π-complex disappears, the ^1H NMR signals due to the DVA π-complex increase, accompanied by a decrease in those due to the MVA complex (Fig. 2b). Although several signals in Fig. 2 are not fully assigned, they are attributed to those due to MVA and DVA π-complexes by comparing the ^1H NMR spectra in Fig. 2 with those of the ^1H NMR 2D spectra of MVA and DVA in the catalyst solution at 323 K (Fig. 3), which are significantly changed from those in H_2O.
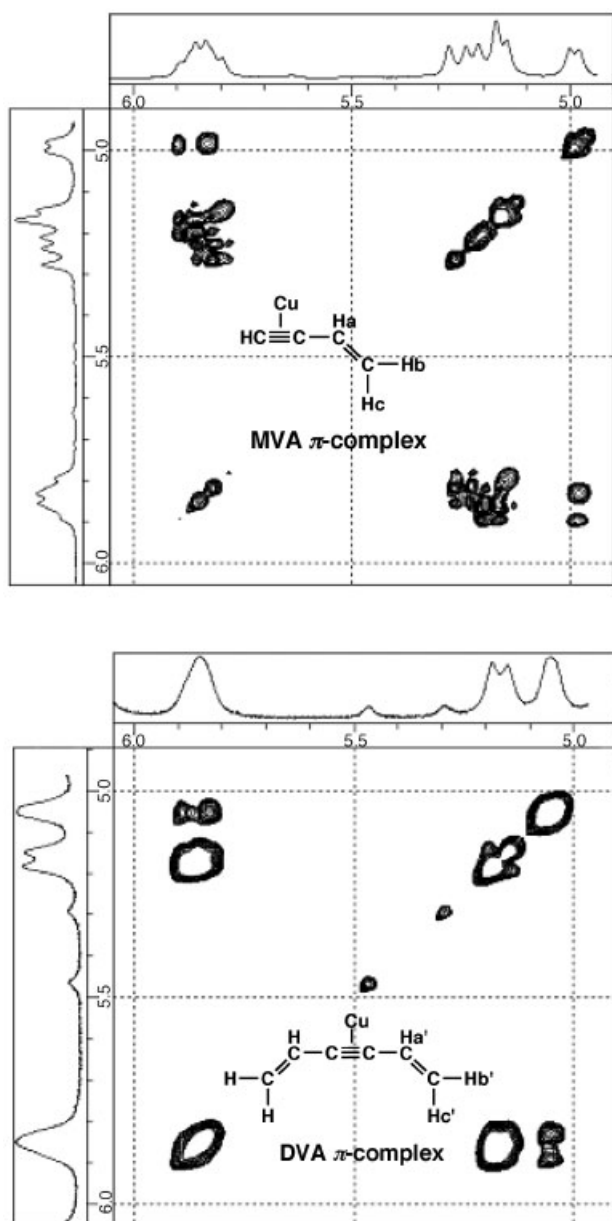
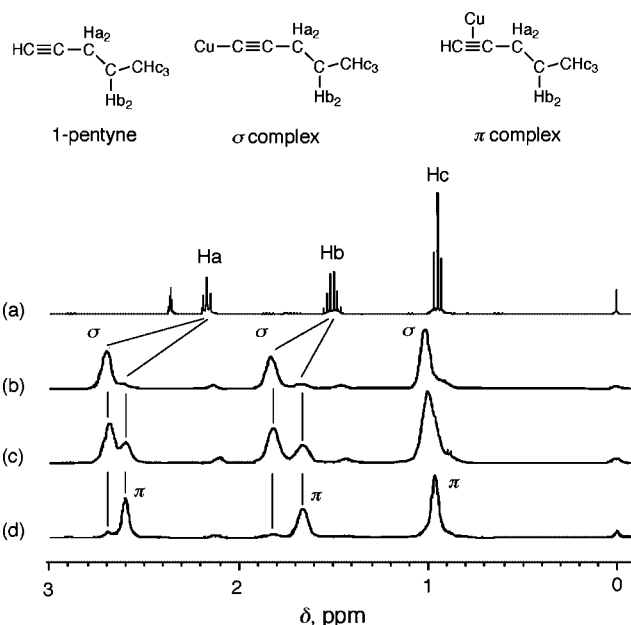**Figure 3.** 2D ^{1}H NMR spectra of MVA and DVA complexes with a Nieuwland catalyst in H_2O at 323 K

Figure 4. ^{1}H NMR spectra of (a) 1-pentyne in D_2O, (b) 1-pentyne in the Nieuwland catalyst solution, and the change in the NMR spectra after addition of (c) 10 mL of DCl and (d) 20 mL of DCl. The Cu–1-pentyne σ-complex is converted to the corresponding π-complex by addition of DCl

No reaction of MVA and DVA takes place in the catalyst solution without acetylene other than the complex formation with the catalyst. The apparent doublet signal at 5.0 ppm due to the MVA complex is readily distinguished from the signal at 5.05 ppm due to the DVA complex. The π-complex formation with the double bond of MVA and DVA is also possible. Although the detailed structures of the π-complexes with the catalyst have yet to be clarified, the π-complexes can readily be distinguished from the σ-complexes (*vide infra*).

In contrast to the case of MVA and DVA, the ^{1}H NMR spectra of 1-pentyne in the catalyst solution exhibit the signals due to both π- and σ-type complexes. The σ-complex is converted to the π-complex by adding DCl to the catalyst solution of 1-pentyne (Fig. 4). There was no such change in the NMR spectra of MVA and DVA in the presence of DCl. This indicates that MVA and DVA form mainly the π-complexes with the catalyst.

Now that the ^{1}H NMR spectra of the MVA and DVA π-complexes are available, we examined the time course of the acetylene dimerization reaction in the catalyst solution by ^{1}H NMR. Acetylene (the flow rate of 360 mL/h) was passed into an NMR tube that contains the Nieuwland catalyst aqueous solution for 3 min. After the NMR tube was sealed, the reaction was monitored at 323 K. The time course of the acetylene, MVA and DVA π-complexes is shown in Fig. 5, indicating that the acetylene π-complex with the Nieuwland catalyst is converted to the MVA π-complex and then to the DVA π-complex by the reaction between the acetylene π-complex and the MVA π-complex. The decay of the acetylene π-complex in H_2O obeys first-order kinetics as shown in the inset of Fig. 5 (open circles). This indicates that a unimolecular reaction of the acetylene π-complex is the rate-determining step of the catalytic dimerization of acetylene.

When H_2O is replaced by D_2O, the ^{1}H NMR signal due to the acetylene π-complex under otherwise the same experimental conditions becomes much smaller as compared with that in H_2O because of the rapid H/D exchange, which converts C_2H_2 to C_2HD and C_2D_2 (*vide supra*). In addition, the first-order decay rate in the D_2O is 3.9 times smaller than that in H_2O. Such a deuterium kinetic deuterium isotope effect is consistent with that observed in the decay rate of acetylene in the gas phase (Fig. 1c).

Based on the results described above, the reaction mechanism of the catalytic H/D exchange reaction and the dimerization of acetylene is proposed as shown in Scheme 3. First, acetylene forms a π-complex with Cu^I species of the Nieuwland catalyst, which is responsible for the rapid H/D exchange reaction between C_2H_2 and D_2O to convert C_2H_2 to C_2HD and C_2D_2 (Scheme 2). After the H/D exchange, the dimerization of C_2D_2 starts via the C_2D_2–Cu^I π-complex (Scheme 3). The C_2D_2–Cu^I π-complex undergoes deprotonation to produce the correspond-

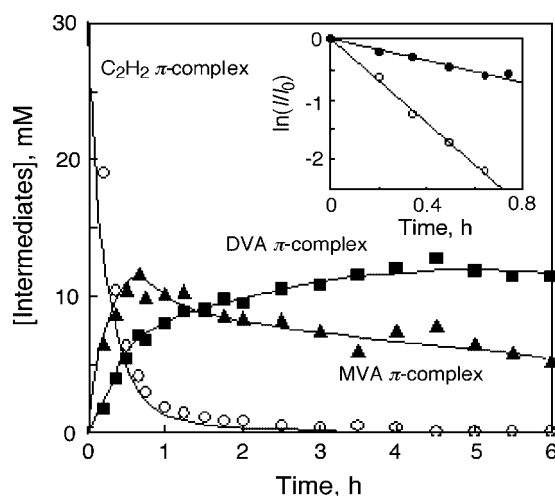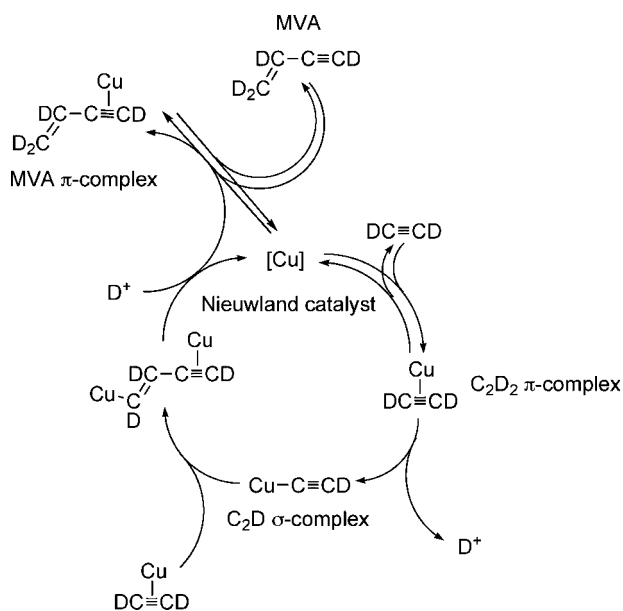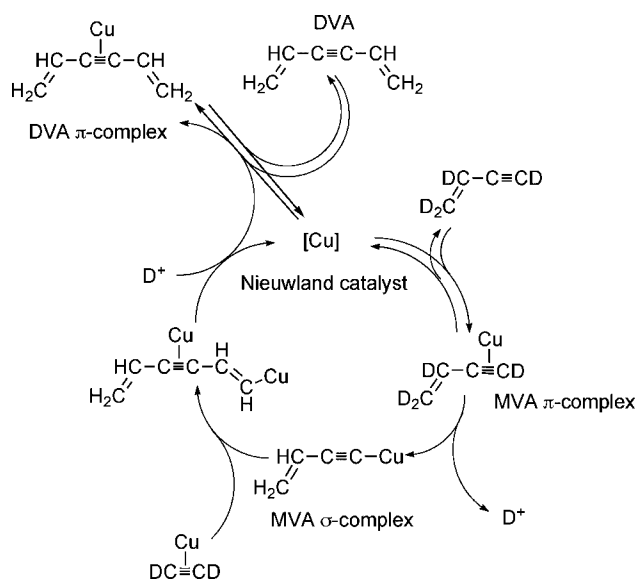**Figure 5.** Time profiles of intermediates in the Nieuwland catalyst solution ([CuCl] = 7.0 M) at 323 K; C_2H_2 π-complex (○), MVA π-complex (▲), and DVA π-complex (■). Inset: First-order plot of the ratio of ^{1}H NMR signal intensity due to the Cu–acetylene π-complex to the initial intensity (I/I_0) in H_2O (○) and D_2O (●)

Scheme 4.

ing σ-complex (C_2D–Cu^I), which is the rate-determining step of the catalytic dimerization of acetylene, exhibiting the deuterium kinetic isotope effect (Fig. 1c). In such a case, the σ-complex cannot be observed during the reaction because the σ-complex reacts with the acetylene π-complex rapidly to yield the MVA π-complex (Scheme 3). No free acetylene is involved in the dimerization step, because all acetylene molecules in the catalytic solution are converted to the acetylene π-complexes (*vide supra*). The dimerization may occur via formation of the σ- and π-complex with the same catalytic site, followed by the reductive elimination as the case of Pd-catalyzed coupling reaction.[4,5] However, the detailed reaction mechanism of the dimerization step has remained to be clarified.

The same catalytic cycle is applied for the formation of DVA starting from the MVA π-complex that reacts with the acetylene

π-complex via the MVA σ-complex to produce the DVA π-complex as shown in Scheme 4. DVA detected in the gas phase is in equilibrium with the DVA π-complex (Scheme 4). Since the time course of the products in the gas phase (Fig. 1) is in parallel with that in the Nieuwland catalytic solution (Fig. 5), the MVA and DVA π-complexes are in equilibrium with MVA and DVA in the gas phase, respectively (Schemes 3 and 4).

CONCLUSIONS

The dimerization of acetylene with a Nieuwland catalyst in an aqueous solution proceeds via formation of the acetylene π-complex, which is responsible for the rapid H/D exchange between acetylene and proton (or deuteron) of water. The deprotonation of the acetylene π-complex to afford the σ-complex with the Nieuwland catalyst is the rate-determining step in the catalytic dimerization of acetylene. In order to optimize the yield of MVA in the gas phase, it is of primary importance to eliminate MVA in the gas phase to avoid the further reaction of the MVA π-complex with the acetylene π-complex, which leads to the formation of a by-product, DVA.

Scheme 3.

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